

Quantum non-equilibrium approach for fast electron transport in open systems: photosynthetic reaction centers

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Creation of electron or exciton by external fields in a system with initially statistically independent unrelaxed vibrational modes leads to an initial condition term. The contribution of this term in the time convolution generalized master equation approach is studied in second order of the perturbation theory in the path integral formalism. The developed approach, applied for analysis of dynamics in the photosynthetic reaction center, exhibits the key role of the initial condition terms at the primary stage of electron transfer.

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I. INTRODUCTION

The effect of environment on transport properties of quantum systems is a highly topical problem in atomic, nuclear and condensed matter physics. Markovian approaches have been successfully used to study various phenomena in open systems, when the past memory of the system is neglected [1]. The advent in ultrafast laser-pulse technology [2], quantum information processing [3], synthesis of new superheavy elements in cold and hot-fusion reactions [4] are requiring a resolution of quantum dynamics, when a system is far from equilibrium.

Analogous processes can be found in biological systems [5] as well as in nanoscale devices [6]. Although there are wide structural and functional differences, the laws, that govern quantum solar energy conversion to chemical energy or electricity in biological systems and semiconductor solar cells, share many similarities. In these systems the conversion processes proceed from the creation of electron-hole pairs (excitons) by a photon of light, followed by charge separation to produce the required high-energy product. The efficiency of solar cells may be increased due enhanced multiple exciton production in semiconductor quantum dots, which is essentially created extremely fast upon absorption of high-energy photons [7]. On the other hand, the photosynthetic reaction center (RC) of bacteria provides an interesting system for studying a high-efficiency electron transfer in an organized molecular complex. The RC is a special pigment-protein complex, that functions as a photochemical trap. In such systems, after excitation the electron transfer is so fast that there can exist unrelaxed vibrational modes in the primary stage of electron transfer.

In a most studied case of a purple bacteria the RC is composed of three protein subunits called L, M and H [8, 9]. According to experimental facts, the protein H does participate in the electron transfer (ET). All molecules (cofactors) involved in the ET are non-covalently bound to subunits L and M in two chains.

Both chains of cofactors start at the bacteriochlorophyll dimer (P) which interacts with both subunits L and M. The dimer plays the role of the donor of an electron (a weakly bound exciton) at the photon absorption. Cofactors in the subunit L are accessory bacteriochlorophyll (B_L), bacteriopheophytin (H_L) and quinone (Q_L). Identically, in the M subunit there are the accessory bacteriochlorophyll (B_M), bacteriopheophytin (H_M) and quinone (Q_M). The cofactors serve as donor-acceptor pairs in the ET. The arrangement of cofactors shows the local twofold symmetry which is almost perfect with the respect to the dimer. The part of the L subunit involved in the ET can be superimposed onto the corresponding part of the M subunit by a rotation of almost exactly 180° (for more details on structural arrangement see [10]).

In spite of the structural symmetry of the two chains of cofactors, it appears that the RC is functionally highly asymmetric. In the primary charge transfer an electron is transferred from the photoexcited dimer P, the starting point for a series of electron transfer reactions across the membrane, to the cofactors on subunit L, to B_L , H_L , Q_L , and Q_M [11, 12]. On the other hand, the chain located on subunit M is inactive in the ET. The highly asymmetric functionality, however, can be decreased by amino acid mutations or cofactor modification [13]. If the direct ET between subunits L and M is not allowed and electron cannot escape from the system then it was shown that the different stochastic fluctuations in the energy of subunits and the interaction between subunits on these two ways may cause the transient asymmetric electron distribution at L and M branches during relaxation to the steady state [14]. However, due to fast electron transfer the memory effects should be important at the primary processes in the photosynthesis. The major goal of the present paper is to elucidate the effect of the initial condition terms on electron transfer in a system with initial conditions being far from equilibrium.

The content of the paper is as follows. In Sec. II we outline the derivation of the generalized master equation adapted for physics of the RC. In Sec. III we use this

equation to analyse the contribution of the initial condition terms on electron transfer in three-site model of the RC. A brief summary is presented in Sec.IV. In Appendix A there are details of the GME equation derivation.

II. MASTER EQUATION FOR REACTION CENTER

Formally, an exact generalized master equation (GME) which describes the electron transfer processes in systems with dissipation can be constructed by means of the projection operator techniques [15, 16]. To be specific let us consider a system in which an electron has N accessible sites embedded in a medium. Such a system is described by the Hamiltonian

$$H = H_0 + V, \quad (1)$$

where $H_0 = \sum_{n=1}^N |n\rangle[\varepsilon_n - i\Gamma_n + H_n^v]\langle n|$. Here, $|n\rangle$ is the electron state with energy ε_n . The parameter $\hbar/2\Gamma_n$ characterizes the electron lifetime at site $|n\rangle$. It may originate, for example, from a nonradiative internal conversion or a recombination process. The term H_n^v describes a medium (a solvent) consisting of harmonic oscillators

$$H_n^v = \sum_{\alpha} \left\{ \frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2}m_{\alpha}\omega_{\alpha}^2(q_{\alpha} - d_{n\alpha})^2 \right\}. \quad (2)$$

Here, $d_{n\alpha}$ is the equilibrium configuration of the α th oscillator, which depends on the electronic state $|n\rangle$. The interaction $V = \sum_{n,m=1}^N V_{nm}|n\rangle\langle m|(n \neq m)$ couples different sites.

The GME formulation of an electron (an exciton) interacting with vibrational modes (phonons) starts from the Liouville equation for a density operator $\rho(t)$ [1]

$$i\frac{\partial}{\partial t}\rho(t) = \frac{1}{\hbar}[H\rho(t) - \rho(t)H^+] \equiv L\rho(t). \quad (3)$$

At this stage the projector operator technique allows to avoid a knowledge of a complete information upon a system under consideration. The projector operator contracts the full information about the system to the relevant one. Our prime interest is the information about the electron localization and the irrelevant information is a particular vibrational state excited in the system. In virtue of this technique [15, 16] one obtains

$$\begin{aligned} \frac{\partial}{\partial t}D\rho(t) = & -iDLD\rho(t) - \\ & - \int_0^t DL \exp[-i(1-D)L\tau](1-D)LD\rho(t-\tau)d\tau - \\ & - iDL \exp[-i(1-D)Lt](1-D)\rho(0) \end{aligned} \quad (4)$$

for the relevant part $D\rho(t)$ of the total density $\rho(t)$. Here $D = D^2$ is an arbitrary linear projection operator which can be used in the form [17]

$$DA = \sum_n Tr(|n\rangle\langle n| A) \rho_n |n\rangle\langle n|. \quad (5)$$

The total trace $Tr = Tr_e Tr_Q$ is a product of traces of the electronic (Tr_e) and the vibrational (Tr_Q) subsystems; $\rho_n = \exp(-\beta H_n^v)/Tr_Q[\exp(-\beta H_n^v)]$ is a density operator for a vibrational subsystem, when an electron is localized at a site $|n\rangle$ ($\beta = 1/k_B T$). Often, the projector operator is chosen in such a way that the initial state $(1-D)\rho(0)$ is disregarded [1]. This approximation is valid when electron and phonon subsystems are initially in equilibrium. Evidently, that at the primary stage of the electron transfer this term may influence the electron pathway in the RC. The questions arise about the time-scale of such influence in the system under consideration and how this influence would affect the ET.

To calculate the initial condition terms we have to specify $\rho(0)$. The photon absorption by the dimer results in the transition of an electron from the ground to the excited state of the dimer (say, the excited state $|1\rangle$). Before the excitation the electronic subsystem is in the thermal equilibrium with the vibrational subsystem which consists in vibrational modes of the dimer and the protein subunits. Due to the fast electron transfer to molecules located in L(M)-branches of the RC the time is too short to establish a thermal equilibrium between the vibrational subsystem and a new electronic state. On the other hand, the vibrational subsystem (the bath) is in the thermal equilibrium with the electronic ground state of dimer. Thus, we have

$$\rho(0) = \rho_0 \otimes \left(\sum_{kl} \rho_{kl}^e(0) |k\rangle\langle l| \right) \quad (6)$$

where $\rho_0 = \exp(-\beta H_0^v)/Tr_Q[\exp(-\beta H_0^v)]$ is a density operator for a vibrational subsystem, when an electron is at the ground state. Here $\rho_{kl}^e(0) = Tr_Q(\langle k|\rho(0)|l\rangle)$ is an electronic part of the density matrix. We suppose that an electron is initially localized on the first molecule: i) $\rho_{11}^e(0) = 1$, $\rho_{nn}^e(0) = 0$, $n = 2, N$; ii) non-diagonal initial density matrix elements are $\rho_{kl}^e(0) = 0$. We also assume that after the excitation the electron transfer is so fast that the initial vibrational density is not affected. Similar assumptions for the construction of the initial state $\rho(0)$ have been used for analysis of the energy transfer dynamics in a model of a donor-acceptor pair [18]. In principle, the initial conditions may be calculated within a scheme proposed to include system-bath correlations after the interaction with optical pulses [19]. However, this problem requires a dedicated study itself in order to distinguish different time scales and is beyond the scope of the present consideration. The main objective here is to gain insights into the role of the initial condition terms on the ET for a few typical cases.

With the aid of Eq.(5) one obtains

$$D\rho(0) = \rho_1 \otimes |1\rangle\langle 1|, \quad (7)$$

which leads to the initial state

$$(1-D)\rho(0) = (\rho_0 - \rho_1) \otimes |1\rangle\langle 1|. \quad (8)$$

Evidently, if the condition $\rho_0 \simeq \rho_1$ is not fulfilled, one must take into account the initial state in Eq.(4).

Substituting Eq.(5) in Eq.(4), one obtains the GME

$$\partial_t P_n(t) = -\frac{2\Gamma_n}{\hbar} P_n(t) - \sum_{m(\neq n)} \int_0^t [ReW_{nm}(t-\tau)P_n(\tau) - ReW_{mn}(t-\tau)P_m(\tau)]d\tau + I_n(t) \quad (9)$$

for site occupation probabilities

$$P_n(t) = Tr (|n\rangle\langle n| \rho(t)) = \rho_{nn}(t) . \quad (10)$$

The first term in the r.h.s. of Eq.(9) is associated with the probability for an electron to escape from the system via an additional channel.

In the Born approximation, the memory function $W_{mn}(t)$ can be expressed in the form

$$W_{mn}(t) = 2 \frac{|V_{mn}|^2}{\hbar^2} \exp\left(-\frac{\Gamma_m + \Gamma_n}{\hbar} t\right) \times \exp\left(i \frac{\varepsilon_m - \varepsilon_n}{\hbar} t\right) \exp\left(\sum_{\alpha} \frac{E_{mn}^{\alpha}}{\hbar\omega_{\alpha}} \times [(\bar{n}_{\alpha} + 1)e^{-i\omega_{\alpha}t} + \bar{n}_{\alpha}e^{i\omega_{\alpha}t} - (2\bar{n}_{\alpha} + 1)]\right). \quad (11)$$

Here $\bar{n}_{\alpha} = [\exp(\hbar\omega_{\alpha}/k_B T) - 1]^{-1}$ is a thermal population of the α th vibrational mode and

$$E_{mn}^{\alpha} = \frac{1}{2} m_{\alpha} \omega_{\alpha}^2 (d_{m\alpha} - d_{n\alpha})^2 \quad (12)$$

is the reorganization energy of the α th vibrational mode, when an electron moves from state $|m\rangle$ to state $|n\rangle$.

In second order of the perturbation theory, one obtains from Eq.(4) the initial condition term (IT) in the form (see also [20, 21])

$$I_n(t) = I_n^{(1)}(t) + I_n^{(2)}(t) \quad (13)$$

where the first order term is

$$I_n^{(1)}(t) = -iTr (|n\rangle\langle n| \mathcal{L}e^{-iL_0 t}(1-D)\rho(0)) \quad (14)$$

and the second order term has the form

$$I_n^{(2)}(t) = - \int_0^t d\tau \Phi(t, \tau). \quad (15)$$

Here,

$$\Phi(t, \tau) = Tr \left(|n\rangle\langle n| \mathcal{L}e^{-iL_0(t-\tau)} \mathcal{L}e^{-iL_0\tau}(1-D)\rho(0) \right) \quad (16)$$

and

$$\mathcal{L}A = \frac{1}{\hbar}[V, A], \quad L_0 A = \frac{1}{\hbar}[H_0, A]. \quad (17)$$

The choice of the initial conditions Eqs.(6),(7), and Eqs.(17) yield

$$I_n^{(1)}(t) = 0. \quad (18)$$

The ITs fulfil the general identity which transforms in the considered case to

$$\sum_n I_n(t) = 0 \Rightarrow I_1^{(2)}(t) = - \sum_{n=2}^N I_n^{(2)}(t). \quad (19)$$

Evidently, the definition of $I_n^{(2)}(t)$ is crucial for the calculation of the GME (9). For $I_n^{(2)}(t)$ we obtain the following expression (see details in Appendix)

$$I_n^{(2)}(t) = Re \int_0^t d\tau W_{1n}(t-\tau) \mathcal{B}, \quad n = 2, \dots, N \quad (20)$$

$$\mathcal{B} = \exp \left[2i \sum_{\alpha=h,v} S_{10}^{\alpha} \mathcal{M}_{\alpha} \right] - 1$$

where the variable S_{10}^{α} (see Eq.(A10)) is determined by the reorganization energy of the α vibrational mode E_{10}^{α} , Eq.(12), when electron moves from the ground state $|0\rangle$ to the excited state $|1\rangle$ of the dimer P. As a check, using the same techniques, we have calculated $I_1^{(2)}(t)$ and obtained the fulfillment of Eq.(19).

Note that if one considers the contribution of the non-diagonal density matrix elements, the first order term contributes to the GME as well [22, 23].

III. MODEL OF PRIMARY STAGE OF ELECTRON TRANSFER IN A REACTION CENTER

To demonstrate the viability and utility of our approach, we consider the electron transfer in RCs within a three-site model. In the RC, after photon absorption at the bacteriochlorophyll dimer molecules (molecule 1) the electron transfer may occur either through the M-side bacteriochlorophyll (molecule 2) or the L-side bacteriochlorophyll (molecule 3) accessors. We assume that there are two non-zero coupling terms V_{12} and V_{13} and a forbidden direct electron transfer between molecules 2 and 3 ($V_{23} = 0$). The two possible electron transfer pathways are related by the C_2 symmetry axis. The pathway symmetry is broken by differences in amino acid around the donor-acceptor pairs in the different branches. These differences inhibit a charge separation through the M-branch in the wild type RC. The preference of the pathway ($1 \rightarrow 3$) relative to the pathway ($1 \rightarrow 2$) is assumed to be governed by the energy differences and by the different couplings between donor-acceptor pairs in the branches. Indeed, experimental and theoretical estimates for the energy differences provide the following figures [24, 25]: $\varepsilon_1 - \varepsilon_3 \approx 0.05 - 0.1$, $\varepsilon_2 - \varepsilon_1 \approx 0.1 - 0.2$ (eV).

The Hamiltonian H_0^v determines the vibrational state, the equilibrium position of the oscillatory mode, and, consequently, the density operator for the vibrational subsystem, when an electron is in the base state of the donor molecule before the excitation. The phonon bath

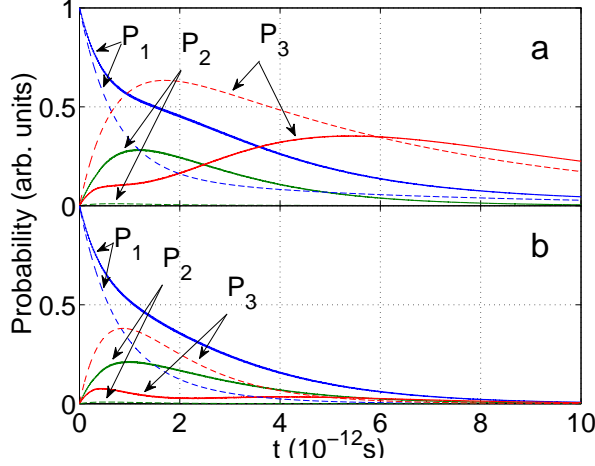


FIG. 1: (Color online) Time dependence of the site occupation probabilities $P_i(t)$. Solid (dashed) lines are used for results with (without) the ITs. The basic parameters are used for the both panels. The specific parameters are: $S_{10}^h = 1, S_{10}^v = 0$; a) $2\Gamma_2/\hbar = 2\Gamma_3/\hbar = (5ps)^{-1}$; b) $2\Gamma_2/\hbar = 2\Gamma_3/\hbar = (1ps)^{-1}$

is described by two vibrational modes, high frequency mode ω_h and low frequency ω_v . The low-frequency mode characterizes the exterior medium phonon mode and the high-frequency mode describes the molecular vibrational modes of the donor and the acceptor centers [26, 27]. We take into account a relaxation time for the vibrational mode $\omega_\alpha \rightarrow \omega_\alpha - i/\tau_\alpha$ with the aid of a phenomenological parameter τ_α (see also [28]). As a result, for numerical analysis the variables (A11), (A12) are considered in the form

$$\mathcal{N}_\alpha = (2\bar{n}_\alpha + 1)[1 - e^{-t/\tau_{p\alpha}} \cos(\omega_\alpha t)] + ie^{-t/\tau_{p\alpha}} \sin(\omega_\alpha t)$$

$$\mathcal{M}_\alpha = \exp(-t/\tau_{p\alpha}) \sin(\omega_\alpha t) - \exp(-\tau/\tau_{p\alpha}) \sin(\omega_\alpha \tau)$$

To illustrate the contribution of the ITs in the ET, we use parameters that may elucidate in the Markovian approximation the observed L-side experimental kinetics of wild-type (WT) RCs of *Rb. sphaeroides* [26, 29]. Note that the probability of the M-side electron transfer was excluded in such considerations.

In particular, the following set of parameters (set I) is used to characterize the electron transfer in a wild type RC via the L branch (the pathway $1 \rightarrow 3$): $V_{13} = 7$ meV, $\hbar\omega_h = 187$ meV, $\hbar\omega_v = 12.5$ meV, $S_{13}^h = 0.5$, $S_{13}^v = 8$ [26]. The same set can be used for the electron transfer via the M branch (the pathway $1 \rightarrow 2$), taking into account that there is a two-fold symmetry. To provide the asymmetry in the electron transfer via the two pathways we consider: $\varepsilon_3 - \varepsilon_1 = -56$ meV and $\varepsilon_2 - \varepsilon_1 = 110$ meV (see discussion in [14]). This choice forms the set II.

Evidently, that the RC is an open system which interacts with another part of overall system. This part can be assumed to have a quasi-continuum spectrum. To

mimic the realistic situation we introduce sink parameters Γ_i/\hbar ($i = 1, 3$) which characterize the electron transfer to another part of the overall system with a quasi-continuum spectrum. This is an effective approach to describe resonance scattering phenomena in open systems with a weak coupling to the environment (see, for example, [30]). When an electron is transferred to this subsystem, the backward electron transfer can be neglected. The primary charge separation step ($1 \rightarrow 3$) occurs in purple bacterial RCs with a lifetime $\sim 2ps$ at room temperature. The next step of electron transfer occurs in the time scale $\sim 1ps$ [31]. In the numerical calculations we have used the following values of sink parameters: $2\Gamma_1/\hbar = (250ps)^{-1}$ [32], $2\Gamma_2/\hbar = 2\Gamma_3/\hbar = (5ps)^{-1}$ and $(1ps)^{-1}$. The parameter $2\Gamma_1/\hbar$ characterizes the decay of the system to the ground state, while $2\Gamma_{2,3}/\hbar$ are associated with the electron transfer to the next molecules (subsystems) which are beyond the scope of the present analysis. The flow direction also depends on the parameter S_{10}^h which characterizes the amount of energy stored in unrelaxed high frequency vibrational modes. The scale reorganization constant values are chosen as $S_{10}^h = 0.5$ and $S_{10}^h = 1$. We take $\tau_\alpha \simeq 3.5ps$ for the lattice relaxation time, in accordance with the observation that a vibrational mode relaxation time is of order a few ps [33]. The set III consists of $2\Gamma_1/\hbar$ and τ . The sets I, II, III form the basic parameters of calculations of occupation probabilities at 300K, shown at Figs.1,2.

Let us consider a case when the lattice relaxation time is smaller than ones defined by the sink parameters (see Fig.1a). The system has time to achieve the regime when the impact of the unrelaxed phonon mode on the occupation probabilities is easing. This imposes the impact of the ITs upon the electron flow direction. The electron flow direction is similar to the one defined by the theory without the ITs. At the early stage of electron transfer the ITs have, however, a strong influence on the quantum yields of the electron flow through different branches. The theory without the ITs predicts that the M branch is inactive. The ITs activates the electron escape through the branch M (molecule 2).

The energy stored in the unrelaxed phonon modes is large ($S_{10}^h = 1$) in this case. The parameters $\hbar/2\Gamma_2 = \hbar/2\Gamma_3 = 5ps$ are large enough in comparison with the phonon relaxation time $\tau_p = 3.5ps$. The system evolves in time to the regime where the ITs influence decreases on the electron transfer (the system begins to forget the initial conditions). Therefore, the flow direction is the same as in the case without the ITs. If the sink parameters are smaller than the phonon relaxation time (see Fig.1b) the ITs change the favourite partway for the electron transfer: the dominance of the pathway ($1 \rightarrow 3$) (without the ITs) is replaced by the dominance of the pathway ($1 \rightarrow 2$) (with the ITs).

Let us consider the regime, when the unrelaxed phonon modes of the medium are taken into account ($S_{10}^v = 2$) (Fig.2). Such amount of the unrelaxed medium modes has no a strong impact on the main characteristic of elec-

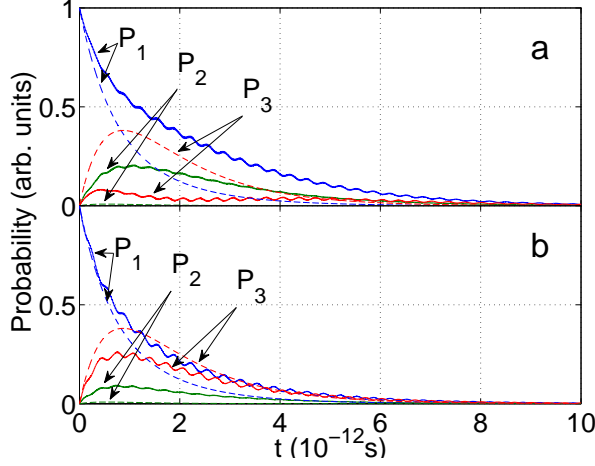


FIG. 2: (Color online) The basic parameters are the same as in Fig.1b. The specific parameters for this figure are: $S_{10}^v = 2$. a) $S_{10}^h = 1$; b) $S_{10}^h = 0.5$.

tron transfer. The medium modes can not store large amount of the unrelaxed energy. Indeed, the transition of the system to the excited state affects rather the rearrangement of atom positions in the donor-molecule and, thus, has no a strong impact on the medium atom positions. The ITs increase the probability for electron transfer via the molecule 2 in comparison to the case without the ITs. The electron lifetime in the system is still short enough not to forget the initial condition. With the decrease of unrelaxed phonon energy in the system (compare Figs.2a,b) the importance of the ITs is also decreasing.

Another important ingredient is the dependence of the results on the ratio of the phonon relaxation time and the time associated with the interaction V . All results discussed above are related to the situation when $\tau > \hbar/V_{1m}$. In this case the electron transitions are fast, while the phonon relaxation is a slow process. The ITs will contribute to the ET depending on the amount of energy stored in the unrelaxed vibrational modes, in accordance with the discussion above. On the other hand, if $\tau \ll \hbar/V_{1m}$ the ITs produce a marginal effect, and the initial conditions are forgotten relatively quickly.

IV. SUMMARY

In conclusion, we suggest the microscopic approach to study the effect of the ITs on the electron transfer in a system with initial conditions being far from equilibrium. The IT impact depends mainly on the amount of energy stored in the initially unrelaxed phonon modes and also on the lifetime of the electron in the system. If the electron lifetime is much longer than the phonon relaxation time, the ITs do not affect the quantum yields of electron transfer via possible pathways. In systems, where

this condition is not fulfilled, the ITs can cause the electron transfer via channels which are closed in the case without the ITs.

Appendix A: Initial condition terms

Let us employ the initial conditions (6),(7), in the definition of the second order of the initial term (15),(16),

$$I_n^{(2)}(t) = \int_0^t d\tau \text{Tr} \left(|n\rangle \langle n| \mathcal{L} e^{-iL_0(t-\tau)} \times \right. \quad (\text{A1}) \\ \left. \times \mathcal{L} e^{-iL_0\tau} (\rho_1 - \rho_0) |1\rangle \langle 1| \right), \quad n = 2, \dots, N.$$

With the aid of Eqs.(17) we obtain

$$I_n^{(2)}(t) = -2\text{Re} \frac{|V_{1n}|^2}{\hbar^2} \int_0^t d\tau \times \quad (\text{A2}) \\ \times \exp \left(-\frac{i}{\hbar} (\varepsilon_n - \varepsilon_1)(t - \tau) \right) \times \\ \times \exp \left(-\frac{1}{\hbar} (\Gamma_n + \Gamma_1)(t - \tau) \right) \times \\ \times \text{Tr}_Q \left(e^{\frac{i}{\hbar} H_1^v t} e^{-\frac{i}{\hbar} H_n^v(t-\tau)} e^{-\frac{i}{\hbar} H_1^v \tau} (\rho_1 - \rho_0) \right)$$

To proceed further it is necessary to calculate the trace over the environmental (vibrational) degrees of freedom, which has, in general, the following form

$$\mathcal{I} = \text{Tr}_Q \left(e^{\frac{i}{\hbar} H_m^v t} e^{-\frac{i}{\hbar} H_n^v(t-\tau)} e^{-\frac{i}{\hbar} H_m^v \tau} \rho_k \right) \quad (\text{A3})$$

In the path integral formalism this trace can be written as

$$\mathcal{I} = \sum_{\nu_\alpha} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dx_1 \times \quad (\text{A4}) \\ \times \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dy_1 \langle k\nu_\alpha | q \rangle \\ \times \langle q | \exp \left(i \frac{H_m^v}{\hbar} t \right) | x_1 \rangle \langle x_1 | \exp \left(-i \frac{H_n^v}{\hbar} (t - \tau) \right) | y \rangle \\ \times \langle y | \exp \left(-i \frac{H_m^v}{\hbar} \tau \right) | y_1 \rangle \langle y_1 | \exp(-\beta H_k^v) | k\nu_\alpha \rangle / \mathcal{Z}.$$

Here, $\mathcal{Z} = \text{Tr}_Q [\exp(-\beta H_k^v)]$ and a vibrational state is

$$\langle q | k\nu_\alpha \rangle = \chi_{\nu_\alpha}(z) = \mathcal{N} \times H_{\nu_\alpha}(z) \exp(-z^2/2) \\ \mathcal{N} = \left(\frac{1}{\ell_0 \pi^{1/2} 2^{\nu_\alpha} \nu_\alpha!} \right)^{1/2}, \quad z = (q - d_{k\alpha})/\ell_0,$$

where $\ell_0 = \sqrt{\hbar/m\omega_\alpha}$ is the oscillator length, and H_{ν_α} is Hermitian polynomial of order ν_α .

In order to obtain an analytical result we suggest to calculate this expression in the integral path formalism [34]. As a result, Eq.(A4) takes the following form

$$\mathcal{I} = \sum_{\nu_\alpha} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dy_1 K_m(q, -t; x_1) \times K_n(x_1, t - \tau; y) K_m(y, \tau; y_1) \chi_{\nu_\alpha}(y_1 - d_{k\alpha}) \times \exp[-\beta(\nu_\alpha + 1/2)\hbar\omega_\alpha] \chi_{\nu_\alpha}(q - d_{k\alpha}), \quad (\text{A5})$$

where

$$K_i(x, t; y) \equiv \langle x | \exp(-iH_i^v t) | y \rangle = \sqrt{\frac{1}{2i\pi\ell_0^2 \sin \omega_\alpha t}} \exp \left\{ i \frac{\mathcal{F}_0}{2\ell_0^2 \sin \omega_\alpha t} \right\} \quad (\text{A6})$$

$$\mathcal{F}_0 = \cos \omega_\alpha t [(x - d_{i\alpha})^2 + (y - d_{i\alpha})^2] - 2(x - d_{i\alpha})(y - d_{i\alpha}). \quad (\text{A7})$$

In virtue of the equation

$$\begin{aligned} \sum_m \chi_m(x - d_0) \exp[-\beta(m + 1/2)\hbar\omega_\alpha] \chi_m(y - d_0) &= \\ = \sqrt{\frac{1}{2\pi\ell_0^2 \sinh(\beta\hbar\omega_\alpha)}} \exp \left\{ - \frac{\mathcal{F}_1}{2\ell_0^2 \sinh(\beta\hbar\omega_\alpha)} \right\} &(\text{A8}) \\ \mathcal{F}_1 = \cosh(\beta\hbar\omega_\alpha) [(x - d_0)^2 + (y - d_0)^2] & \\ - 2(x - d_0)(y - d_0) & \end{aligned}$$

we obtain

$$\mathcal{I} = \exp \left\{ - S_{mn}^\alpha \mathcal{N}_\alpha \right\} \exp \left\{ 2i S_{mk}^\alpha \mathcal{M}_\alpha \right\}, \quad (\text{A9})$$

$$S_{mn}^\alpha = E_{mn}^\alpha / \hbar\omega_\alpha, \quad (\text{A10})$$

$$\mathcal{N}_\alpha = (2\bar{n}_\alpha + 1)(1 - \cos \omega_\alpha(t - \tau)) + i \sin \omega_\alpha(t - \tau), \quad (\text{A11})$$

$$\mathcal{M}_\alpha = \sin \omega_\alpha t - \sin \omega_\alpha \tau. \quad (\text{A12})$$

Taking into account the definitions (A2), (11), with the aid of Eq.(A9), for $m = 1$ we obtain the result (20).

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